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(54) PRODUCTION OF 2-IMIDAZOLINE COMPOUND

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject compound without by-producing hydrogen sulfide, easy in the recovery of catalysis, and not causing the corrosion of a device by reacting a diamine compound with a nitrile compound in the presence of a metal oxide and a carboxylic acid as the catalysts.

SOLUTION: A method for producing a 2-imidazoline compound comprises reacting (A) a 1,2-diamine compound, preferably a 1,3-diamine compound of the formula: $H_2HCHR_1CHR_2NHR_3$ (R_1 to R_3 are independently H, an aliphatic group, an aromatic-aliphatic group, an aromatic group), with (B) a nitrile compound, preferably a nitrile compound of formula: R_4CH (R_4 is the same as R_1 to R_3) in the presence of (C) a metal oxide (preferably zinc oxide, niobium oxide, chromium oxide, manganese oxide) and a carboxylic acid. For example, ethylene as the component A is reacted with acetonitrile as the component B in the presence of active zinc powder and acetic acid as the component C to obtain 2-methylimidazole. The active zinc powder is not dissolved in the acetic acid and can be recovered.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacturing method of imidazoline.

[0002]

[Description of the Prior Art] The following approaches are learned by manufacture of 2-imidazoline which uses a diamine compound and a nitril compound as a raw material.

[0003] The approach of making it react under existence of sulfur is indicated by JP,39-24965,B. When a toxic high hydrogen sulfide carried out the byproduction of the approach of making sulfur a catalyst extremely during a reaction and also an imidazole was manufactured from imidazoline, the sulfur which remains carried out poisoning of the nickel of a catalyst, and it had the problem of checking a reaction.

[0004] In order to solve this problem, the approach of making it as copper salt catalysts, such as copper acetate and a copper chloride, at JP,5-39943,B, and making a catalyst zinc salt, such as zinc acetate and a zinc chloride, at JP,62-195369,A is indicated. If salts, such as copper acetate and zinc acetate, are used, since a catalyst will dissolve in reaction mixture, recovery of a catalyst is difficult and a catalyst pollutes a product. Moreover, when the chloride of copper and zinc is used, the corrosion of the equipment produced for chloride ion poses a problem.

[0005]

[Problem(s) to be Solved by the Invention] The recovery of a catalyst for which the purification which checks the reaction in which a hydrogen sulfide carries out a byproduction is needed and which equipment corrosion starts has problems, such as difficulty, and the conventional approach is hard to be referred to as having reached sufficient level. Therefore, development of the approach which does not make a salt a catalyst and does not carry out the byproduction of the hydrogen sulfide was desired.

[0006]

[Means for Solving the Problem] As a result of examining the manufacturing method of imidazoline wholeheartedly, by using a metallic oxide and a carboxylic acid as a catalyst, this invention persons do not have generating of a hydrogen sulfide, either, recovery of a catalyst is also easy the persons, and they do not have a problem of the contamination and corrosion which are produced when a salt catalyst is used, find out the new fact that manufacture of imidazoline is possible, and came to complete this invention.

[0007] That is, in case this invention makes 1 and 2-diamine compound and a nitril compound react and manufactures 2-imidazoline, it is the manufacturing method of 2-imidazoline characterized by carrying out under existence of a metallic oxide and a carboxylic acid.

[0008] This invention is explained further below at a detail.

[0009] The catalysts used in the approach of this invention are a metallic oxide and a carboxylic acid. As a metallic oxide said in the approach of this invention For example, an aluminum oxide, a silicon dioxide, titanium oxide, a vanadium oxide, Chromic oxide, manganese oxide, ferrous oxide, cobalt oxide, nickel oxide, Although oxidization copper, a zinc oxide, an oxidization yttrium, a zirconium dioxide, niobium oxide, molybdenum oxide, the silver oxide, cadmium oxide, indium oxide, oxidization tin, tantalum oxide, tungstic oxide, rhenium oxide, lead oxide, a lanthanum trioxide, cerium oxide, etc. are mentioned Since activity selectivity improves also in it, oxidization copper, chromic oxide, manganese oxide, a zinc oxide, and especially niobium oxide are desirable. Although there are copper(I) oxide and copper(II) oxide in copper oxide, whichever may be used and a copper hydroxide as well as an oxide can be used. A hydroxide can be similarly used about zinc and niobium. Moreover, copper oxide may be supported and used for support. As support,

multiple oxides, such as oxides, such as a silica and an alumina, and a silica alumina, activated carbon, porous glass, porous ceramics, etc. can be used.

[0010] Moreover, a metallic oxide can be used even if it mixes with other metallic oxides. For example, a copper chromite, a copper oxide-zinc oxide, etc. can be used.

[0011] Although there is especially no limit in a carboxylic acid, formic acid, an acetic acid, a propionic acid, butanoic acid, An isobutyric acid, a valeric acid, an isovaleric acid, a pivalic acid, a lauric acid, a myristic acid, Aliphatic series saturation monocarboxylic acid, such as a palmitic acid, stearin acid, and 2-ethylhexanoic acid Oxalic acid, a malonic acid, an amber acid, a glutaric acid, an adipic acid, a pimelic acid, Aliphatic series saturation dicarboxylic acid, such as a suberic acid, an azelaic acid, and a sebacic acid An acrylic acid, a propiolic acid, a methacrylic acid, a crotonic acid, isocrotonic acid, Oleic acid, an elaidic acid, a maleic acid, a fumaric acid, a citraconic acid, Aliphatic series unsaturated carboxylic acid, such as mesaconic acid, **** of ****, a benzoic acid, A phthalic acid, isophthalic acid, a terephthalic acid, a naphthoic acid, a toluic acid, Heterocycle type carboxylic acids, such as ring type carboxylic acids, such as hydratropic acid, an atropic acid, and a **** leather acid, a full acid, a ten acid, a nicotinic acid, and an isonicotinic acid, monochloroacetic acid, dichloroacetic acid, trifluoroacetic acid, etc. are illustrated. However, in order to make it a catalyst not affect product purity, it is desirable to use the carboxylic acid corresponding to the nitril of a raw material. For example, when an acetonitrile is used as a raw material, it is good to use an acetic acid as a catalyst.

[0012] Moreover, even if it uses a carboxylic-acid compound in the form of a salt, it does not interfere at all.

[0013] There is especially no limit in the ratio of a metallic oxide and a carboxylic acid. Only with a carboxylic acid or a metallic oxide, although a reaction is slow, if both exist, a reaction will be accelerated greatly.

[0014] In addition, on the conditions in the approach of this invention, since a diamine compound exists, it becomes strong base nature, a metallic oxide and a carboxylic acid react, and the inside of a system does not form a salt.

[0015] The raw materials used in the approach of this invention are 1 and 2-diamine compound and a nitril compound. 1 and 2-diamine compound is a compound shown by the formula (1), and is $H_2NCHR_1CHR_2NHR_3$. (1)

(R₁, R₂, and R₃ mean among a formula one or more sorts chosen from the group which consists respectively independently of a radical of hydrogen, aliphatic series, aroma aliphatic series, and aromatic series)

A nitril compound is a compound shown by the formula (2).

[0016]

R_4CN (2)

(R₄ means the radical of hydrogen, aliphatic series, aroma aliphatic series, or aromatic series among a formula)

As a 1 and 2-diamine compound, for example Ethylenediamine, propylenediamine, Butylene diamine, pentene diamine, hexylene diamine, octylene diamine, Nonylene diamine, decylene diamine, cyclohexyl ethylenediamine, Benzyl ethylenediamine, phenylethylene diamine, methoxypheny ethylenediamine, Dimethylphenyl ethylenediamine, tolyl ethylenediamine, N-cyclohexyl ethylenediamine, N-benzyl ethylenediamine, N-phenylethylene diamine, N-methoxypheny ethylenediamine, N-dimethylphenyl ethylenediamine, N-tolyl ethylenediamine, etc. are illustrated.

[0017] Moreover, as a nitril compound, an acetonitrile, propionitrile, isobutyronitrile, 2-ethyl HEKISHIRO nitril, RAURO nitril, SUTEARO nitril, cyclohexyl nitril, phenylacetone nitrile, phenyl propionitrile, a benzonitrile, a methyl benzonitrile, dimethylbenzo nitril, methoxybenzo nitril, dimethylbenzo nitril, naphth nitril, a cyano pyridine, chestnut nitril, an adiponitrile, phthalonitrile, dicyano diphenyl, etc. are illustrated, for example. 1 and 2-diamine compound and a nitril compound can react by one [the chemical equivalent or] excess.

[0018] In the approach of this invention, although reaction temperature is usually performed in 100-300 degrees C for improvement in a reaction rate, decomposition control of amines, and the improvement in yield of imidazoline, it is still more desirable to carry out at 150-250 degrees C.

[0019] The approach of this invention is usually enforced by the liquid phase.

[0020] In the approach of this invention, a reaction can be performed under ordinary pressure or pressurization that what is necessary is just to be able to keep a raw material liquefied. At this reaction, in order that ammonia may generate during a reaction, reaction pressure rises, but this ammonia is also removable in the middle of a reaction, and after a reaction is completed, it is also removable. When reaction temperature is over the boiling point of a raw material, it is necessary to react under pressurization, or to form a condenser and to liquefy a raw material.

[0021] In the approach of this invention, even if it uses a solvent, it is not necessary to carry out. Use is not desirable, although there will be especially no limit and water etc. will decompose imidazoline as a solvent, if inactive to a reaction condition.

[0022] The approach of this invention may be enforced by the successive reaction, and may be enforced at a batch reaction and a half-batch reaction. Moreover, it can react also to the fixed bed or the suspension floor. According to a reaction format, that what is necessary is just to choose the optimal thing, the gestalt of a catalyst may be used with powder, and it may be used, casting.

[0023] In the approach of this invention, even if the imidazoline of a resultant refines, the dehydrogenation of it is carried out without refining, and it is good also as an imidazole. Although various approaches, such as distillation and recrystallization, are learned, even if the purification approach of imidazoline uses which approach, it does not interfere at all.

[0024]

[Example] Hereafter, although an example explains this invention, this invention is not limited to these.

[0025] the autoclave made from stainless steel of 1200ml of examples -- ethylenediamine: -- after putting in and carrying out the nitrogen purge of 60.1g, acetonitrile:45.2g, active white:3g, and the acetic-acid:1.5g, it heated at 200 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 3 hours. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 99% and the selectivity of 2-methyl imidazoline was 98%. In addition, the active white did not dissolve after reaction termination in reaction mixture, but were collected.

[0026] It reacted by the same approach as an example 1 except having used active white:4.5g and having not used an acetic acid as example of comparison 1 catalyst. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 14% and the selectivity of 2-methyl imidazoline was 82%.

[0027] It reacted by the same approach as an example 1 except having used acetic-acid:4.5g and having not used an active white as example of comparison 2 catalyst. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 22% and the selectivity of 2-methyl imidazoline was 71%.

[0028] the autoclave made from stainless steel of 2200ml of examples -- ethylenediamine: -- after putting in and carrying out the nitrogen purge of 60.1g, acetonitrile:45.2g, active white:1.5g, and the acetic-acid:1.5g, it heated at 180 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 5 hours. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 97% and the selectivity of 2-methyl imidazoline was 96%. In addition, the active white did not dissolve after reaction termination in reaction mixture at all, but were collected.

[0029] As example of comparison 3 catalyst, it reacted by the same approach as an example 2 except having used zinc acetate:3g. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 92% and the selectivity of 2-methyl imidazoline was 96%. In addition, it dissolved in reaction mixture after reaction termination, and zinc acetate was not able to be collected.

[0030] the autoclave made from stainless steel of example 31L -- ethylenediamine: -- after putting in and carrying out the nitrogen purge of 75.1g, acetonitrile:226g, active white:7.5g, and the acetic-acid:7.5g, it heated at 180 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 2 hours. It was supplied with the pump, having ethylenediamine 225.4 bet it on this for 5 hours. After maintaining at 180 degrees C after that for 2 hours, when this was cooled and gas chromatography analyzed, the ethylenediamine invert ratio was 98% and the selectivity of 2-methyl imidazoline was 97%.

[0031] the autoclave made from stainless steel of 4200ml of examples -- ethylenediamine: -- after putting in and carrying out the nitrogen purge of 60.1g, acetonitrile:45.2g, manganese oxide addition copper chromite:3g, and the acetic-acid:1.5g, it heated at 200 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 3 hours. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 90% and the selectivity of 2-methyl imidazoline was 94%.

[0032] It reacted by the same approach as an example 1 except having used copper chromite 4.5g and having

not used an acetic acid as example of comparison 4 catalyst. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 51% and the selectivity of 2-methyl imidazoline was 97%.

[0033] the autoclave made from stainless steel of 5200ml of examples -- ethylenediamine: -- after putting in and carrying out the nitrogen purge of 60.1g, acetonitrile:45.2g, niobium oxide:3g, and the acetic-acid:1.5g, it heated at 200 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 3 hours. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 98% and the selectivity of 2-methyl imidazoline was 98%.

[0034] the autoclave made from stainless steel of 6200ml of examples -- 1,2-propanediamine: -- after putting in and carrying out the nitrogen purge of 74.1g, acetonitrile:45.2g and copper(II) oxide:3g, and the acetic-acid:1.5g, it heated at 200 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 3 hours. When this was cooled after reaction termination and gas chromatography analyzed, the 1,2-propanediamine invert ratio was 95%, and the selectivity of 2-methyl-4-methyl imidazoline was 93%.

[0035] the autoclave made from stainless steel of 7200ml of examples -- ethylenediamine: -- after putting in and carrying out the nitrogen purge of 60.1g, propionitrile:60.6g, niobium oxide:3g, and the propionic-acid:1.5g, it heated at 200 degrees C. When reaction pressure was set to 2.5 or more MPas, depressuring was carried out, the pressure was lowered and it reacted for 3 hours. When this was cooled after reaction termination and gas chromatography analyzed, the ethylenediamine invert ratio was 99% and the selectivity of 2-ethyl imidazoline was 92%.

[0036]

[Effect of the Invention] This invention does not have generating of a hydrogen sulfide, either, and recovery of a catalyst is also easy this invention, it offers the manufacture approach of the imidazoline the problem of contamination by the ion produced when a salt catalyst is used, and corrosion is also incomparable, and is very significant.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacturing method of 2-imidazoline characterized by carrying out under existence of a metallic oxide and a carboxylic acid in case 1 and 2-diamine compound and a nitril compound are made to react and 2-imidazoline is manufactured.

[Claim 2] The approach according to claim 1 characterized by expressing 1 and 2-diamine compound with a degree type.

H₂NCHR₁CHR₂NHR₃ (1)

(R₁, R₂, and R₃ mean among a formula one or more sorts chosen from the group which consists respectively independently of a radical of hydrogen, aliphatic series, aroma aliphatic series, and aromatic series)

[Claim 3] The approach according to claim 1 or 2 characterized by expressing a nitril compound with a degree type.

R₄CN (2)

(R₄ means the radical of hydrogen, aliphatic series, aroma aliphatic series, or aromatic series among a formula)

[Claim 4] The approach according to claim 1 to 3 characterized by reacting by the liquid phase.

[Claim 5] The approach according to claim 1 to 4 characterized by a metallic oxide being copper oxide.

[Claim 6] The approach according to claim 1 to 4 characterized by a metallic oxide being a zinc oxide.

[Claim 7] The approach according to claim 1 to 4 characterized by a metallic oxide being niobium oxide.

[Claim 8] The approach according to claim 1 to 4 characterized by a metallic oxide being chrome oxide.

[Claim 9] The approach according to claim 1 to 4 characterized by a metallic oxide being manganese oxide.

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